(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 806 653 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
05.09.2001 Bulletin 2001/36

(51) Int Cl.[7]: **G01N 21/85**, G01N 21/53, G01N 21/35

(21) Application number: **97107459.6**

(22) Date of filing: **06.05.1997**

(54) Method of analyzing material undergoing a change in optical density

Verfahren zur Analyse eines Materials, dessen optische Dichte sich ändert

Procéé d'analyse d'un matériau subissant un changement de densité optique

(84) Designated Contracting States:
DE FR GB

(30) Priority: **09.05.1996 US 647247**

(43) Date of publication of application:
12.11.1997 Bulletin 1997/46

(73) Proprietor: **Perstorp Analytical, Inc.**
Silver Spring, Maryland 20904 (US)

(72) Inventor: **VonBargen, Kenneth P.**
Berwyn Heights, Maryland 20740 (US)

(74) Representative:
DIEHL GLAESER HILTL & PARTNER
Patentanwälte
Königstrasse 28
22767 Hamburg (DE)

(56) References cited:
EP-A- 0 540 035
WO-A-93/06458
WO-A-96/12174
US-A- 5 044 755

- **ANALYTICAL CHEMISTRY, vol. 65, no. 3, 1 February 1993, ISSN 0003-2700, pages 287-292, XP002036929 LIN J ET AL: "Near-IR fiber-optic probe for electrolytes in aqueous solution "**

EP 0 806 653 B1

Description

Field of Invention

[0001] The present invention relates to a method according to the introductory part of claim 1. The invention is particularly suited to the in situ analysis of pharmaceutical compositions which undergo *significant* physical changes during a batch manufacturing process.

Background of the Invention

[0002] Spectrometric analysis is a non-invasive and non-destructive manner in which to determine both qualitative and quantitative properties of compositions. Infrared analysis and more particularly near-infrared ("NIR") analysis, is particularly suited to the analysis of organic compounds. The infrared absorption spectrum is highly characteristic, and is sometimes referred to as the molecular fingerprint. The natural vibrational frequencies of molecules and crystals fall within the infrared range and therefore the infrared region is valuable for the study of the structure of matter. Certain molecular bonds are prone to vibrate when exposed to characteristic wavelengths of infrared radiation which causes the molecules to absorb infrared radiation. Near infrared spectroscopy takes advantage of this activity by measuring the absorption of an unknown sample at various wavelengths throughout the near infrared range. Infrared light which is either reflected from or transmitted through a sample exhibits a highly characteristic spectrum showing the absorption of the sample at various predetermined wavelengths. The wavelength and magnitude of the absorption, as revealed in a spectrograph (a graphical representation of the absorbance values), can be used to determine information about the molecular structure and composition of the sample. Infrared spectrometry has proven to be a valuable tool for analysis of a wide variety of products including milk, grains, oils, gasoline, alcohols, and pharmaceutical products.

[0003] When measuring substances which are harmful or explosive it is often desirable to use an optical probe to interface with the sample. The probe can be directly inserted into a sample of gas or liquid which reduces the possibility of adverse exposure to the technician. In general, measuring devices used for infrared spectroscopy require a near infrared light source and a light detector contained in an instrument known as a spectrometer. Light which has been either reflected from or transmitted through a sample is broken down into narrow wavelength bands either before or after interaction with the sample. In conventional arrangements, fiber optic cables transmit the light to and from the sample in a probe which provides an appropriate interface with the sample. The narrow wavelength bands are then directed to a light detector which then transmits a signal indicative of the intensity of light. The signal is then analyzed or interpreted to yield absorbance data which in turn provides information about the constituent make-up of the sample.

[0004] Absorbance measurements are generally either reflective, transmission or transflectance. Reflectance measurements involve directing light at a sample and then collecting the light which is reflected either from the surface of a sample or from molecules or crystals contained within a sample. A portion of the light reflected from the sample is directed back to a light sensitive detector system where it is converted to a signal. In the detection operation, the output of the photodetectors is sampled at predetermined times corresponding to narrow wavelength bands to yield values which indicate the intensity of the reflected light at the bands. The analysis of reflectance measurements involves scanning a standard, often in the form of a white reflective tile. The value of the signal generated from light reflected from the standard is compared with the light reflected from the sample to yield a value representing the absorbance of the sample. Reflectance measurements are routinely employed in the measurement of solids and non-Newtonian matter such as chemical powders and solid agricultural products.

[0005] A second type of infrared analysis is referred to as transmittance or transmission which involves directing infrared light at a sample and then measuring the light which has passed through the sample. This operation requires a probe to transmit the light and an optical receiver to collect light. Incident light which has passed through the sample is collected by the receiver and is directed to a detector. The detector then generates a signal from which absorbance values of the substance being analyzed are determined. As in the case of reflectance measurements, an absorption spectrum can be created which sets forth the absorbance of the sample plotted as a function of wavelength. Transmittance measurements also require a standard or reference measurement which approximates 100 percent transmittal of radiation. Usually the reference measurement is taken with an empty sample cell or a cell containing a clear liquid. The value of the signal from light transmitted through the sample is compared with the value of the signal obtained from the standard to yield an absorbance value. Because of the limits to the instruments sensitivity, transmission absorption spectra is generally limited to samples which are relatively transparent to infrared radiation.

[0006] A third, hybrid method of spectrometric measurement is referred to as transflectance which involves the simultaneous collection of both light which has been reflected from and light transmitted through a sample. This method also involves providing an illuminating source which transmits infrared radiation to a probe immersed within the sample. Sample material can flow into a gap provided on the end of the probe which is defined by a window and,an opposite mirror. Light is transmitted from the probe through the window and then through the sample where it impinges on the mirror. From the mirror

light is reflected back again through the sample and back through the window where it is collected by suitable means, such as an optical fiber, and directed to a detector. In this arrangement, some of the light falls directly on matter suspended within the sample and consequently is scattered by the sample. A portion of the scattered light is directly reflected back to the collection fiber. Thus, in certain circumstances, the collection fiber captures both light which has been transmitted through the sample and reflected from the sample. Although the amount of radiation reflected from the sample is dependant on the composition of the sample, typically the reflective values from fluid samples are low. As a result, conventional transflectance instruments are designed to optimize the light which has been transmitted through the sample. Accordingly, in conventional transflectance systems the output from the detectors is measured according to a protocol designed for transmission measurements and thus the absorption values are determined by comparison to transmission standards and constants.

[0007] In the prior art (WO-A-9612174) it is known to provide probes having adjustable path lengths in connection with reflectivity, transflectance and transmission measurements. One recognized advantage of an adjustable transmission probe is to narrow the path length when measuring samples which are relatively opaque to infrared light to optimize the amount of light which will pass through the sample. By providing an instrument with an adjustable path length, absorbance measurements can be kept within the optimum ranges for a given instrument. Using a probe having an adjustable path length further facilitates the technician to take a series of measurements of the sample, each at different path lengths. By comparing the results of the absorption values, errors due to problems with the instrument, such as fouling of the windows of the probe by a film, can be obviated.

[0008] Many of the prior art probes require the removal of the probe from the sampled material in order to change the path length. When dealing with materials which are highly toxic, carcinogenic, radioactive, flammable, at extremely high temperatures or pressures or undergoing a chemical reaction, it is apparent that it is desirable to be able to adjust the path length from a remote location, outside the reaction chamber.

[0009] The technical problem of the present invention is how to accomodate an increase in opacity, or optical density, when monitoring a material undergoing a physical or chemical change, thus providing a probe having an adjustable gap which can be adjusted to precise distances from a location outside a reaction chamber in connection with making spectroscopy measurements.

[0010] Prior art probes exhibit some difficulties when measuring samples which are viscous. For example, some manufacturing processes involve an initial stage which is characterized by a solid suspended within a liquid. During the manufacturing process, the mixture is eventually put into solution and may become transparent. However, in the initial phases of such a process, the mixture to be monitored may resemble a thick opaque slurry. Such mixtures are often heated and agitated to facilitate the formation of a clear solution from the suspension. In other manufacturing processes the opposite sequence occurs -- a relatively transparent or translucent liquid with low viscosity becomes very viscous and virtually opaque to infrared light. Such conditions are frequently manifested in the manufacture of pharmaceutical products. It is desirable to monitor the progress of such processes in order to optimize reaction conditions or otherwise control the operating parameters. However because of the significant changes in the process and because of the presence of the some stages which involve a mixture which is opaque and very viscous, measurements are physically difficult to accomplish. In circumstances where the fluid becomes a thick slurry it is both difficult to ensure fluid will flow within the window gap provided on conventional probes and to collect sufficient light which has passed through the sample to make accurate measurements. In the past when a sample mixture was presented in such conditions the probes or infrared measurement systems would no longer be functionally employed. Despite the potential to employ information using reflectivity measurements in such circumstances, their use has been ignored or overlooked.

Summary of the Invention

[0011] The instant invention involves a method of infrared analysis designed for in situ monitoring of batch type reactions or processes. An apparatus useful for this method according to claim 1 employs an infrared light source, a transflectance probe, a grating, an infrared light detector which generates a signal and a signal analyzer. Infrared light is directed from the light source to a sensing head of the probe by an optical fiber. The sensing head of the probe, designed to be completely immersed within the reactant material, has a window and mirror which can be moved with respect to each other to correspondingly adjust the path length where the sample interfaces with the light. Precise control of the path length can be performed from a location remote from the reaction chamber. The probe contains optical fibers which collect light which has been either transmitted through or reflected from the sample and directs the light to a grating where the light is divided into its constituent wavelengths bands in the NIR range. From the grating infra-red light is directed towards a detection device which generates a signal in response to the intensity of the light. Signals from the detection device are analyzed according to either reflectivity or transmissivity protocols. The respective protocols are predetermined and involve different calibrations. They are dependent on the specific reaction or process which is to be monitored and measured and the criteria governing the protocol is developed from historical data using analytical

methods. The transflectance probe is designed to allow the user to adjust the path length to a maximum position where substantially no radiation is transmitted through the sample when the process is in a viscous and relatively opaque condition. Thus the probe can function in both a reflectivity mode, a transmission or a transflectance mode.

[0012] According to the invention a method of analyzing material undergoing a change in optical density using a near infrared spectrophotometer comprising a probe defining a sample area between a mirror and a fiber optic bundle for transmitting infrared light to said sample area and receiving reflected light from said area, wherein the path length for infrared light in a material in said sample area between said mirror and said fiber optic bundle is adjustable, comprises immersing said probe in said material to introduce said material into said sample area, and making a transmission measurement on said material in said sample area while said material is relatively transmissive with said path length adjusted to a relatively first narrow distance; the infrared light being reflected from said mirror to collecting fibers in said fiber optic bundle in said transmission measurement. Then a reflectivity measurement is made on said material while said material is relatively opaque with said path length adjusted to a second distance wider than said first distance, said second distance being sufficiently wide that essentially no light is transmitted through said material, said reflectivity measurement being analyzed in accordance with a reflectivity protocol.

[0013] When the optical density of said material changes from relatively transmissive to relatively opaque between said measurements said transmission measurement is made before said reflectivity measurement.

[0014] When said material changes from relatively opaque to relatively transmissive between said measurements said reflectivity measurement is made before said transmission measurement.

[0015] When the viscosity of said material changes between said measurements with the viscosity being greater when said reflectivity measurement is made than said transmission measurement is made.

[0016] In a preferred method according to the invention said reflectivity measurement is made with the path length adjusted to its maximum distance.

Brief Description of the drawings:

[0017] Fig. 1 is a schematic plan view of the optical measuring system useful for the method according to the invention.

[0018] Fig. 2 is a side sectional view of the probe assembly useful for the method according to the invention.

[0019] Fig. 3 is a side sectional view of the probe tip.

[0020] Fig. 4 is an end view of the tip of the probe showing the cavity which receives a reflective surface.

[0021] Fig. 5 is another side sectional view of the outer housing showing the housing in engagement with the tip of the probe.

[0022] Fig. 6 is a side view in elevation of the retainer assembly, the pin, the outer housing and tip of the probe.

[0023] Fig. 7 is a bottom sectional view of the inner tubular member and window assembly of the probe.

[0024] Fig. 8a is a front view in elevation of the pin which engages the tubular member of the probe.

[0025] Fig. 8b is a top view in elevation of the pin shown in Fig. 8a.

[0026] Fig. 8c is a side view in elevation of the pin shown in Figs. 8a and 8b.

Detailed Description of the Preferred Embodiments

[0027] Referring now to Fig. 1, the apparatus useful for the method according to the invention has a near-infrared ("NIR") light source 10 which sends a continuous beam 11 of infrared radiation past a shutter 12 where it can impinge on either the end of optical fiber bundles 14 or bundle 16. The light source 10, shutter and the respective fiber optic bundle ends are contained by an enclosure 13. Operation of the shutter controls the NIR light to impinge on either illuminating fiber bundle 14 or reference bundle 16. The shutter 12 can be closed to prevent all NIR light from entering the instrument. The shutter is operated in response to a command from the central processing unit 20 located within an optical enclosure 26.

[0028] The fiber optic bundle 14 provides a link or conduit to transmit infrared light from the NIR source 10 to a probe generally designated by reference numeral 18. The probe 18 provides an interface with the sample material 22 which is to be analyzed. A third bundle of collection optical fiber 24 originates in probe 18 and terminates adjacent to fiber optic bundle 16 inside the optical enclosure 26 of the instrument. The third fiber optic bundle 16 serves as a reference fiber and guides light from the source directly to the optical enclosure. The arrangement can thus be characterized as a split beam which provides infrared light at a relevant value which can be compared against the light which interacts with the sample. Accordingly any fluctuations in the intensity of the light source 10 can be appropriately accounted for in the analysis operation. The reference fiber also eliminates the need for a standard in the reflective mode because the fiber can serve as a surrogate for a reflective standard.

[0029] Now referring to Fig. 2, the probe consists of an outer cylindrical housing 30 having a smooth interior bore which receives an inner tubular member 32. Inner tubular member 32 surrounds a fiber optic bundle which contains both the illuminating fibers and the collecting fibers all of which terminate at a window 34. Window 34 is comprised of sapphire or other suitable material which is both impervious to the sample material and can otherwise withstand the environment of the reaction chamber. Sapphire is characterized by good chemical inert-

ness and excellent transmission properties, particularly for near-infrared wavelengths and is the preferred material for the window. In axial alignment with window 34 is a mirror 36. Mirror 36 is also formed of sapphire and has a surface coated with an appropriate reflective material such as gold to reflect infrared light back to the collecting fibers. Window 34 and mirror 36 define the sample area 38 which, as discussed in more detail below, can be adjusted by sliding the inner tubular member 32 towards the mirror. The sample area is the location into which a sample material can flow and can be subjected to infrared light. Mirror 36 is held in a fixed position with respect to the outer housing 30 and is positioned on a removable tip 40 of the probe 18.

[0030] As best seen in Fig. 3, tip 40 has threads 42 on the exterior surface designed to engage opposite treads on housing 30. An annular cavity 44 is slightly chamfered and designed to precisely receive mirror 36. Transversely, intersection tip 40 is a slot which effectively defines the maximum area through which the sample can flow. The axial dimension of the slot is approximately 20,3 mm. Fig. 4, an axial view of the tip, shows that the bottom of the slot is defined by a flat surface 48 and the slot generally has a rectangular profile which allows fluid to freely pass into the sample area in a direction perpendicular to the axis of the probe.

[0031] Now referring to Fig. 5, a bottom view of the housing, shows an ovular opening 50 on the top of the cylindrical sidewall. Fig. 5 further shows the housing in engagement with the tip. Threads 54 are provided on the interior surface of one end of the cylindrical housing which engage threads of the tip. On the end opposite the tip, threads 52 are provided on the outside surface of the housing which engage a casing 60 as further shown in Fig. 6.

[0032] Fig. 6 shows a pin 56 which serves to limit the axial movement of the tubular member 2 within the housing 30 and prevents rotational movement with respect to the housing 30. The pin is received within ovular opening 50 and is formed so that it does not protrude beyond the exterior surface of the housing and thus the housing can be received unimpeded within casing 60. The pin remains in a fixed position. Figs. 8a-c further show the construction of the pin which is formed by a head 62 which has an arcuate profile which mirrors the curve formed by the cylindrical walls of the outer housing. A shank 64 extends perpendicular to the axis defined by the housing and protrudes into the tubular passage section defined by the housing. Now referring to Figs. 8a-8c, the shank 64 of the pin is designed to be received in the elongate slot 74 provided on the top surface of the inner tubular member 32. The slot 74 is illustrated in Fig. 7. The engagement of the pin within the slot 74 prevents the inner tubular member 32 from rotating within the housing and limits the axial movement of inner tubular member with respect to the housing. Window 34, which provides for the interface between the infrared light and the sample is secured to the end of the tubular member 32 and thereby caps and seals the inner tubular member which contains the optical films. On the opposite end of the inner tubular member 32 a threaded passage 71 is formed perpendicular to the axis which can receive a bolt. The bolt secures the fiber optic bundles (not shown) which lead to and from the window 34.

[0033] Now referring back to Fig. 1 both the reference fiber 16 and the sample fiber 24 are directed to a mirror 68 which directs both the infrared light which has interfaced with the sample and the light which has been collected directly from the source to a grating 70. The grating disperses the infrared radiation into a spectrum and directs specific wavelengths of light to a detector 72 in response to the oscillation of the grating. According to Fig. 1, a post-dispersive grating monochrometer is employed however, it is contemplated that other manners of dispersal would also be effective. For example, the infrared radiation could be divided into bands before interacting with the sample. Adjacent to the light path between grating 70 and detector 72 are standards 74 which can be periodically positioned into the light path when the instrument is instructed by the central processing unit to perform measurements using a protocol for transmission measurements. The standards 74 may be positioned in the path of light in response to a command from a central processing unit 20 at predetermined times. Before reaching the detector 72 the light may also be filtered through an appropriate order sorter filter 76 so that higher order wavelengths are removed. The order sorter filter 76 is also controlled by central processing unit 20 to coordinate the interposition of the correct filter for the wavelength which is passing from the grating to the detector.

[0034] As the grating 70 oscillates, light for each wavelength impinges on the detector 72 a signal is created which reflects the intensity of the light. The electric signal generated by a photodetector is transmitted to an analyzer which translates the signal into useful information regarding the absorbance properties of the sample. Application of an algorithm to the signal interprets quantitative and qualitative aspects of the sample. It is contemplated that other types of analysis could be employed including artificial intelligence techniques or intuitive analysis by experts who can analyze graphical representations of the data by comparing the unknown data with the graphs of known compounds.

[0035] In order to operate the instrument, it first must be calibrated and the constants of appropriate algorithms must be determined. This operation involves making measurements of the process with the instrument at a series of intervals while simultaneously physically removing a sample of the material undergoing the process. The sample is then analyzed by traditional analytical chemistry methods -- eg. NMR, titration, or use of specific reagents. The results of the analytical tests are then correlated to the infrared scans taken at the time of the sample and a mathematical model is created.

This procedure is referred to as the reference step which is repeated a number of iterations throughout several processes in order to obtain accurate data for a number of reference runs. During the reference runs the path length of the probe is set at different distances which is also recorded and each spectrum is correlated with the results from the analytical testing to provide values for the respective spectrums. For each given manufacturing process, a data base or a calibration sample set is created. Then a mathematical process is employed, such as a multi-variant regression analysis or mulfilineal regression, to correlate the signature of the unknown spectrum to the known values and determine constants for algorithm to analysis material being processed. The instrument thus provides an output which may reflect both qualitative and quantitative information regarding the material.

[0036] The measurement with the instrument involves immersing the tip or sensing head of the probe into the sample which is undergoing either a chemical and physical change. If the process is one in which the early stages of the process is a fluid in the nature of an opaque suspension which is going into solution, the operator initially operates the probe in a reflectance mode. Thus, referring to Fig. 2, the adjustment disk 31 is rotated to position mirror 36 at its maximum distance away from the window 34. This distance is measured by an electronic gauge and the value is provided as input to the central processing unit when a command is provided to scan the sample. At the maximum path length, the sample material can readily flow into the gap and essentially no transmission through the sample occurs. In response to the command to scan the sample, the shutter 12 is opened and a full spectrum of near-infrared light is directed in sequence through the fibers. At alternating time intervals, the full infrared spectrum is also directed through the reference fiber. In order to ensure that fluctuations in the intensity of the light source 10 do not adversely effect the measurement, the absorption or reflectivity values is determined by comparing the values of the signal generated from collection fiber from the value determined from the reference fiber. The use of the reference fiber eliminates the need for measurements from both a reflective tiles as is customarily practiced in conventional reflectivity measurement and from an empty sample chamber cell as used in conventional transmissivity measurements.

[0037] During the initial phases of the measurement as described above the constants used in the algorithm which determine the quantitative and qualitative data selected from those previously stored for the measurement at the same time and gap distance. When the reaction has progressed to a point that the reactant mixture becomes relatively transparent, transmission measurements are carried out by rotation of adjustment ring 31 to narrow the path length. The width of the path is narrowed to the degree permitted by the viscosity to enable an effluent transmission to be made. Rotation of the adjustment ring engages the threads 52 on the outer surface of the housing 30 and draws the housing towards the casing 60 and towards a seat 80 found on a flange section of the inner tubular member 32. As the housing 30 is moved towards the seat the mirror 36 approaches window 34. As the mirror approaches the window, the path length is decreased. The mirror and window can be adjusted to precise distances with respect to one another which are detected by the gauge.

[0038] In connection with processes characterized by initial stages which are transparent or translucent, the instrument is initially operated according to conventional transmission procedures. As the reaction progresses, the sample material becomes thick and virtually opaque to NIR light. At this juncture, measurement of the process can proceed by opening the gap of the pore to its maximum width and employing a reflectivity measurement protocol.

[0039] The advantages of the invention which integrates past measurement methodologies are immediately apparent. While the measurements of analogous processes in the past may have required the use of multiple probes, the present invention employs a single probe which is used throughout a complete transformation of a material. A separate reflectivity probe, with its concomitant standards and instrument which in the past may have been used when the reactant mixture is unsuitable for transmission measurements is no longer necessary. Using a single probe and instrument has the obvious advantage of decreasing the costs associated with installation of the instrument on the reaction vessel and the costs of the instruments themselves.

Claims

1. A method of analyzing material undergoing a change in optical density using a near infrared spectrophotometer comprising a probe (18) defining a sample area (22) between a mirror (36) and a fiber optic bundle (14, 24) for transmitting infrared light to said sample area and receiving reflected light from said area, wherein the path length for infrared light in a material in said sample area between said mirror and said fiber optic bundle is adjustable, said method comprising immersing said probe in said material to introduce said material into said sample arca, making a transmission measurement on said material in said sample area while said material is relatively transmissive with said path length adjusted to a relatively first narrow distance; the infrared light being reflected from said mirror to collecting fibers in said fiber optic bundle in said transmission measurement, characterized by: making a reflectivity measurement on said material while said material is relatively opaque with said path length adjusted to a second distance wider than said first distance, said second distance being sufficiently wide

that essentially no light is transmitted through said material, said reflectivity measurement being analyzed in accordance with a reflectivity protocol.

2. A method as recited in claim 1, wherein the optical density of said material changes from relatively transmissive to relatively opaque between said measurements and said transmission measurement is made before said reflectivity measurement.

3. A method as recited in claim 1, wherein said material changes from relatively opaque to relatively transmissive between said measurements and wherein said reflectivity measurement is made before said transmission measurement.

4. A method as recited in claim 1, wherein the viscosity of said material changes between said measurements with the viscosity being greater when said reflectivity measurement is made than when said transmission measurement is made.

5. A method as recited in claim 1, wherein said reflectivity measurement is made with the path length adjusted to its maximum distance.

Patentansprüche

1. Verfahren zum Analysieren von Material, dessen optische Dichte geändert wird, unter Verwendung eines Spektralphotometers für den nahen Infrarotbereich, welches eine Sonde (18) aufweist, die einen Probenbereich (22) zwischen einem Spiegel (36) und einem Glasfaserbündel (14, 24) zum Übertragen von Infrarotlicht zu dem Probenbereich und Empfangen von reflektiertem Licht von dem Bereich definiert, wobei die Weglänge für Infrarotlicht in einem Material in dem Probenbereich zwischen dem Spiegel und dem Glasfaserbündel einstellbar ist, wobei das Verfahren umfasst, die Sonde in das Material einzutauchen, um das Material in den Probenbereich einzuführen, eine Übertragungsmessung an dem Material in dem Probenbereich vorzunehmen, während das Material relativ durchlässig bei Einstellung der Weglänge auf einen relativ schmalen ersten Abstand ist; wobei das Infrarotlicht von dem Spiegel zu Sammelfasern in dem Glasfaserbündel bei der Übertragungsmessung reflektiert wird, **dadurch gekennzeichnet**, dass eine Messung von Reflexionsvermögen an dem Material vorgenommen wird, während das Material relativ undurchlässig bei Einstellung der Weglänge auf einen zweiten Abstand ist, der breiter als der erste Abstand ist, wobei der zweite Abstand ausreichend breit ist, dass im wesentlichen kein Licht durch das Material übertragen wird, wobei die Messung von Reflexionsvermögen entsprechend einem Reflexionsvermögensprotokoll analysiert wird.

2. Verfahren nach Anspruch 1, bei dem sich die optische Dichte des Materials von relativ durchsichtig zu relativ undurchsichtig zwischen den Messungen ändert, und die Übertragungsmessung vor der Messung von Reflexionsvermögen durchgeführt wird.

3. Verfahren nach Anspruch 1, bei dem sich das Material von relativ undurchsichtig zu relativ durchsichtig zwischen den Messungen ändert und bei dem die Messung von Reflexionsvermögen vor der Übertragungsmessung durchgeführt wird.

4. Verfahren nach Anspruch 1, bei dem die Viskosität des Materials sich zwischen den Messungen ändert, wobei die Viskosität größer ist, wenn die Messung von Reflexionsvermögen durchgeführt wird, als wenn die Übertragungsmessung vorgenommen wird.

5. Verfahren nach Anspruch 1, bei dem die Messung von Reflexionsvermögen bei Einstellung der Weglänge auf ihren maximalen Abstand durchgeführt wird.

Revendications

1. Procédé d'analyse d'un matériau subissant un changement de densité optique par utilisation d'un spectrophotomètre fonctionnant dans l'infrarouge proche et comprenant une sonde (18) définissant une zone d'échantillon (22) entre un miroir (36) et un faisceau de fibres optiques (14, 24) pour transmettre de la lumière infrarouge à la zone d'échantillon et recevoir de la lumière réfléchie de la zone, dans lequel la longueur du trajet de la lumière infrarouge dans un matériau dans la zone d'échantillon entre le miroir et le faisceau de fibres optiques est réglable, procédé dans lequel on immerge la sonde dans le matériau pour introduire le matériau dans la zone d'échantillon, on effectue une mesure de transmission sur le matériau dans la zone d'échantillon alors que le matériau est dans un état de transmission relative avec ladite longueur de trajet réglée à une relativement faible distance, la lumière infrarouge étant réfléchie par le miroir vers des fibres réceptrices du faisceau de fibres optiques dans la mesure de transmission, caractérisé par le fait qu'on effectue une mesure de réflectivité sur le matériau alors que le matériau est relativement opaque avec la longueur du trajet réglée à une seconde distance plus grande que la première distance, la seconde distance étant suffisamment grande pour que sensiblement pas de lumière ne soit transmise à travers le matériau, la mesure de réflectivité étant analysée selon un protocole de réflectivité.

2. Procédé selon la revendication 1, dans lequel la densité optique du matériau passe d'un état de transmission relative à un état d'opacité relative entre les mesures et la mesure de transmission est effectuée avant la mesure de réflectivité.

3. Procédé selon la revendication 1, dans lequel le matériau passe d'un état d'opacité relative à un état de transmission relative entre les mesures et dans lequel la mesure de réflectivité est effectuée avant la mesure de transmission.

4. Procédé selon la revendication 1, dans lequel la viscosité du matériau change entre les mesures, la viscosité étant plus élevée lorsqu'est effectuée la mesure de réflectivité que lorsqu'est effectuée la mesure de transmission.

5. Procédé selon la revendication 1, dans lequel la mesure de réflectivité est effectuée alors que la longueur du trajet est réglée à sa distance maximale.

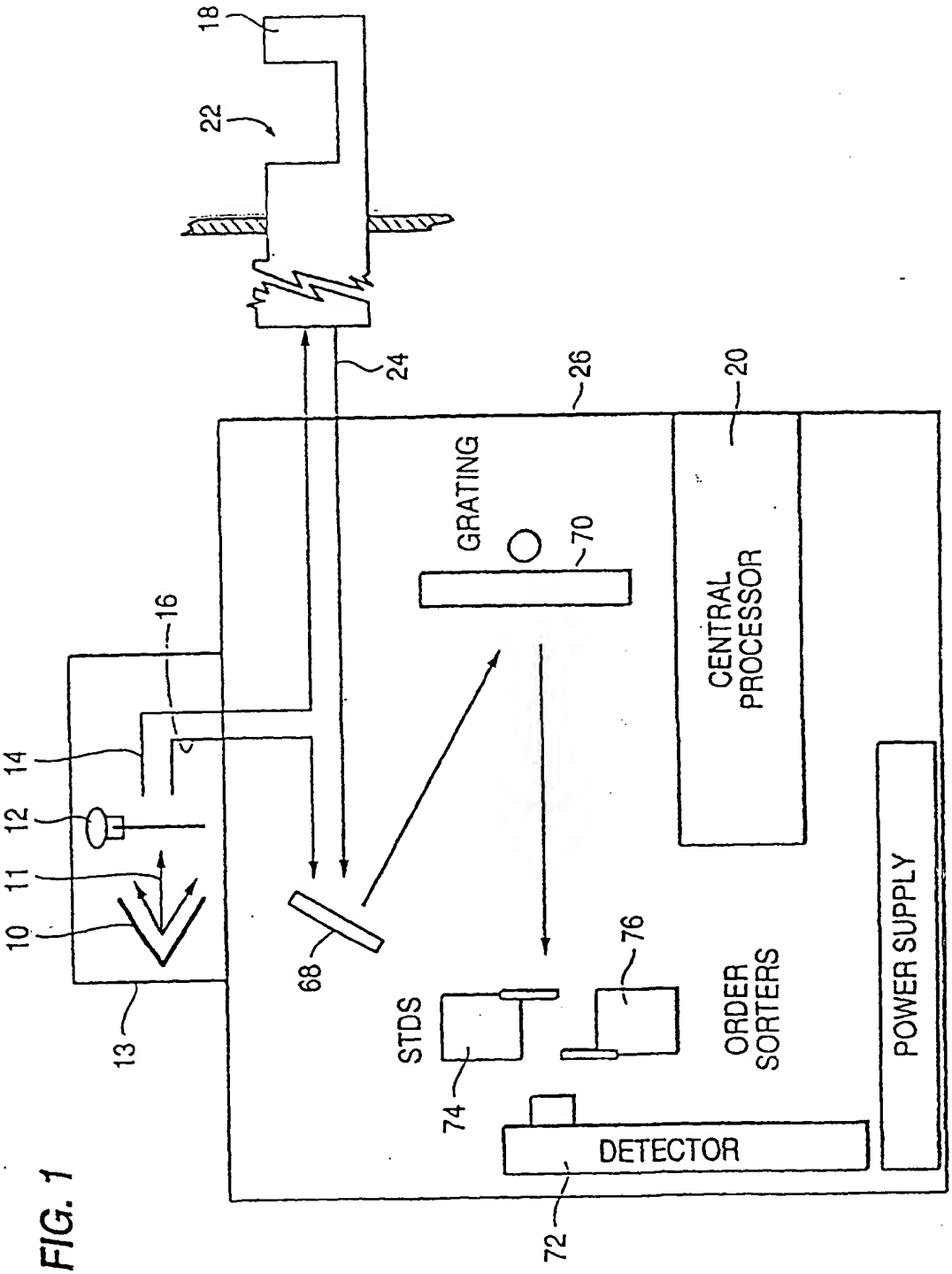

18
22
24
26
20
GRATING
70
CENTRAL PROCESSOR
16
14
12
11
10
13
68
STDS
74
76
ORDER SORTERS
POWER SUPPLY
DETECTOR
72

FIG. 1

FIG. 2

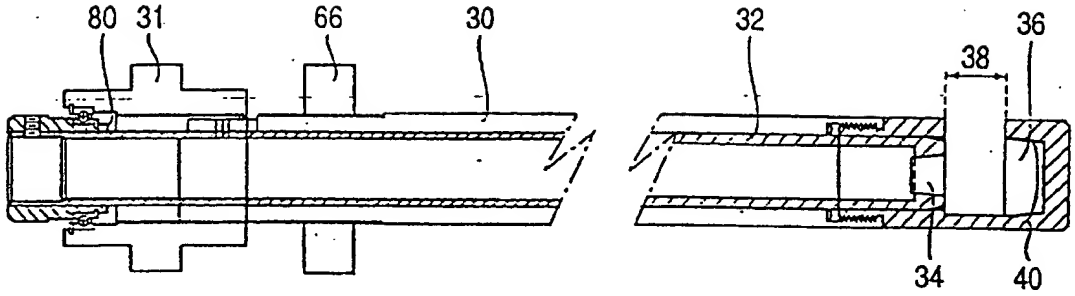


FIG. 3

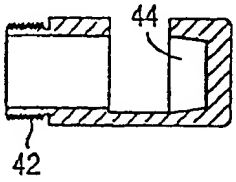


FIG. 4

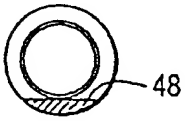


FIG. 5

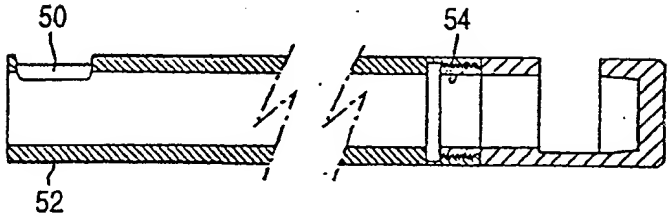
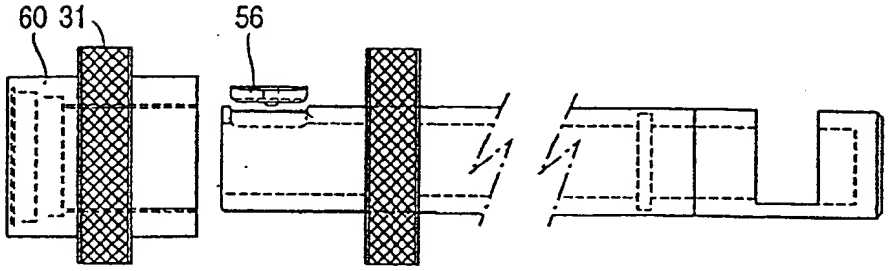


FIG. 6



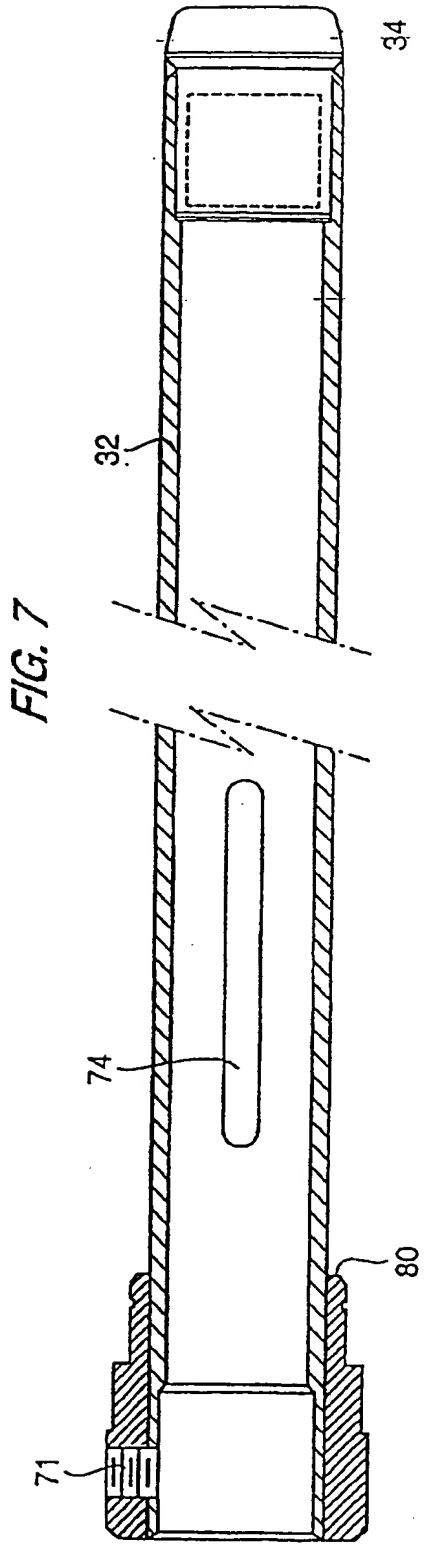


FIG. 7

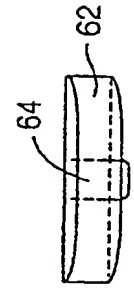


FIG. 8c

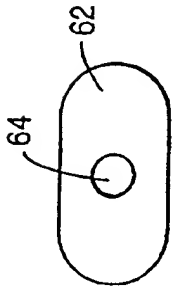


FIG. 8b

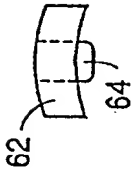


FIG. 8a